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(54) Hairspray Compositions

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ABSTRACT OF THE DISCLOSURE

An aqueous hair treatment composition is provided that includes a water-soluble polymer having a solution viscosity at 10% in water of less than about 20,000 cps at 25°C, and a latex of water-insoluble polymeric particles dispersed in water, the average particle size being no higher than about 2 microns, the latex particles being formed from respective monomers in the presence of the water-soluble polymer.

HAIRSPRAY COMPOSITIONS5 BACKGROUND OF THE INVENTIONField of the Invention

The invention relates to hairspray compositions especially formulated for use in low organic volatile systems.

10

Related Art

Hairspray compositions must meet a number of functional requirements. These include good holding ability and curl retention without giving a harsh, brittle feeling to the hair. Even under humid conditions there must be good hold and curl retention. Another requirement is that the hairspray be capable of being removed upon washing the hair at the time of shampooing. Additionally, the compositions must include the properties of low stickiness and a lack of powdering or flaking.

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Various resins have been employed in hairspray compositions to achieve the aforementioned desirable properties. Illustrative of such resins are the copolymers of vinylpyrrolidone with vinyl acetate, available commercially under such trademarks as Luviskol VA 73 by the BASF Corporation and homopolymers of vinylpyrrolidone commercialized under the trademark PVP K-30 by ISP Corporation. Typical of this art are disclosures in U.S. 3,800,033 (Flawn et al) and U.S. 4,173,627 (Madrange nee Dermain et al). A higher molecular weight homopolymer of vinylpyrrolidone, PVP K-90 Resin trademark of ISP Corporation, is disclosed in U.S. 4,874,604 (Sramek). The aforementioned polymeric resins are of the anionic variety.

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Amphoteric resins have also been extensively employed. These polymers contain cationic radicals derived from monomers such as t-butyl aminoethyl methacrylate as well as carboxyl radicals derived from monomers such as acrylic acid or methacrylic acid. Representative of this group is a product manufactured by the National Starch and Chemical Corporation under the trademark Amphomer identified on product labels by the CTFA name of Octylacrylamide/Acrylates/Butylaminoethyl Methacrylate Copolymers. Use of Amphomer alone or in conjunction with other resins for hairsprays has been reported in U.S. 3,927,199 (Micchelli et al), U.S. 4,402,977 (Grollier et al), U.S. 4,859,455 (Nowak, Jr. et al), U.S. 4,871,529 (Sramek), U.S. 4,983,383 (Maksimowski et al), U.S. 4,983,418 (Murphy et al), U.S. 5,021,238 (Martino et al), GB 2 098 624 (Madrangle) and Canadian Patent 1 222 461 (Varco).

Anionic polymeric resins have also been utilized in this art. For instance, U.S. 4,300,580 (O'Neill et al) discloses linear polyesters prepared from isophthalic acid, the sodium salt of 5-sulfoisophthalic acid and diethylene glycol. Eastman AQ

Polymers for water-dispersed hairsprays are based on this technology. Other polyester and sulfo substituted polymer systems are described in U.S. 4,525,524 (Tung et al).

Environmental concerns and legislation addressing such concerns have required product reformulations to meet these challenges. Organic solvent-based sprays must, at least in part, now be substituted by water systems. Concentrations of organic propellants present in these water systems must also be adjusted to relatively low levels. With these constraints, certain problems have arisen. Water-dispersed

systems are slow to dry. Not only do they result in wetness on the hair but there is also an undesirable coolness sensation that imparts a chill. Quite significantly there is also difficulty in developing the style. Resins formulated in a water-dispersed system can have weak holding power.

Some systems such as the Eastman AQ Resins have good setting or holding but removability from hair is quite poor because these resins are not water soluble.

Furthermore, there is the problem of providing a uniform spray particle size with water-dispersed resins. A still further problem is that of improving glossiness to counteract resins that usually tend to dull hair.

Recently there has been disclosed in a US Patent 5,068,099 (Sramek) an aerosol hairspray package claiming reduced volatile organic compound emission during the useful life of the package. The spray composition contains a combination of at least two polymers differing in weight average molecular weight by at least 1.5. This blend of polymers combines with a low delivery rate discharge mechanism to provide an atomized composition with mean particle size of at least 60 average microns. A significant drawback of this technology is the necessity for very substantial amounts of volatile alcohol; water is present at levels no higher than 10% by weight. Instead of eliminating volatiles from the formula, the patent merely controls the spray emission thereof. However, at some point in the life cycle of the package, volatiles will be emitted into the atmosphere. A further problem with this system is the relatively low rate of spray. It would be desirable to utilize systems with much higher spray rates.

Accordingly, it is an object of the present invention to provide a hairspray suitable for water-based systems having improved holding and styling characteristics.

5 Another object of the present invention is to provide a hairspray composition based on a water-based system that dries fairly quickly and does not impart an undue wetness or cool feel to hair or scalp.

10 A further object of the present invention is to provide a hairspray composition for water-based systems that improves glossiness of the hair.

15 A still further object of the present invention is to provide a hairspray composition for water-based systems that can be sprayed as relatively uniform particles.

20 These and other objects of the present invention will become more evident from the following summary and detailed description.

SUMMARY OF THE INVENTION

An aqueous hairspray composition is provided including:

- 5 (i) a water-soluble polymer having a solution viscosity at 10% in water of less than about 20,000 cps at 25°C, the polymer being present in an amount from about 1 to about 30% by weight; and
- 10 (ii) a latex of water-insoluble polymeric particles dispersed in water, the average particle size being no higher than about 3 microns, the particles being present in an amount from about 1 to about 30% by weight and wherein the water-insoluble polymeric particles are formed from respective monomers in the presence of the water-soluble polymer.

15 In a further aspect of the invention, a method for setting hair is also provided wherein the water-soluble polymer and the latex of water-insoluble polymeric particles are applied to the hair, preferably through spray application.

20 Compositions of this invention are best prepared by forming the latex polymeric particles from appropriate monomers in the presence of the water-soluble polymer in an aqueous medium.

25 Hairspray compositions of this invention are dispersed in water which may contain from 0-50% of a propellant such as dimethyl ether.

DETAILED DESCRIPTION

It has been discovered that many of the objects of the present invention can be achieved through a hair treatment composition that includes a water-soluble polymer having a solution viscosity of less than about 20,000 cps at 25°C when 10% of polymer is placed in water, and a latex of water-insoluble polymeric particles. The latex and water-soluble polymer interact with one another to provide an overall superior hairsetting composition.

According to the invention a wide variety of water-soluble polymers are suitable for use in the composition. These polymers should have a viscosity of less than about 20,000 cps at 25°C when 10% is placed in water, more preferably a viscosity of less than about 10,000 cps. The amount of the polymer may range from about 1 to 30%, preferably from about 1.5 to 10% by weight of the hairspray composition.

The water-soluble polymer may be selected from nonionic, anionic, cationic or amphoteric type hair fixative polymers. However, in systems where the latex particles are anionic, the water-soluble polymer should not be cationic so as to avoid clumping.

Examples of anionic hair fixative polymers are the copolymers of vinyl acetate and crotonic acid, terpolymers of vinyl acetate, crotonic acid and a vinyl ester of an alpha-branched saturated aliphatic monocarboxylic acid such as vinyl neodecanoate; copolymers of methyl vinyl ether and maleic anhydride (molar ratio about 1.1) wherein such copolymers are 50% esterified with a saturated alcohol containing from 1 to 4 carbon atoms such as ethanol or butanol; and acrylic copolymers, terpolymers, etc., containing acrylic acid or methacrylic acid as the anionic



radical-containing moiety and esters of acrylic or methacrylic acid with one or more saturated alcohols having from 1 to 22 carbon atoms such as methyl methacrylate, ethyl acrylate, ethyl methacrylate, n-butyl acrylate, t-butyl acrylate, n-butyl methacrylate, t-butyl methacrylate, n-butyl methacrylate, n-hexyl acrylate, n-octyl acrylate, lauryl methacrylate and behenyl acrylate, glycols having from 1 to 6 carbon atoms such as hydroxypropyl methacrylate and hydroxyethyl acrylate, styrene, vinyl caprolactam, vinyl acetate, acrylamide, alkyl acrylamides and methacrylamides having 1 to 8 carbon atoms in the alkyl group such as methacrylamide, t-butyl acrylamide and n-octyl acrylamide, and other compatible unsaturated monomers. One specific example is the emulsion polymerized terpolymer of methacrylic acid, n-butyl acrylate and ethyl acrylate (e.g., in a weight percent ratio of 31:42:27, respectively). Another specific example is Ultrahold® 8 (CTFA-Cosmetic, Toiletries and Fragrance Association-designation of Acrylate/Acrylamide Copolymer).

Amphoteric polymers which can contain cationic groups derived from monomers such as t-butyl aminoethyl methacrylate as well as carboxyl groups derived from monomers such as acrylic acid or methacrylic acid can also be used in the present invention. One specific example of an amphoteric hair fixative polymer is Amphomer® sold by the National Starch and Chemical Corporation.

Examples of nonionic hair fixative polymers are homopolymers of N-vinylpyrrolidone and copolymers of N-vinylpyrrolidone with compatible nonionic monomers such as vinyl acetate and terpolymers of ethyl acrylate, butyl methacrylate and methyl methacrylate. Nonionic polymers containing N-vinylpyrrolidone in various weight average molecular weights are available commercially from ISP Corporation such

as homopolymers of N-vinylpyrrolidone having an average molecular weight of about 630,000 sold by ISP (formerly GAF Corporation) under the tradename PVP K-90 and those having an average molecular weight of about 1,000,000 sold under the trademark of PVP K-120.

Examples of cationic hair fixative polymers are copolymers of amino-functional acrylate monomers such as lower alkylaminoalkyl acrylate or methacrylate monomers such as dimethylaminoethyl methacrylate with compatible monomers such N-vinylpyrrolidone, vinyl caprolactam, or alkyl methacrylates such as methyl methacrylate and ethyl methacrylate and alkyl acrylates such as ethyl acrylate and n-butyl acrylate. Cationic hair fixative polymers containing N-vinylpyrrolidone are commercially available from ISP Corporation such as those sold under the trademarks of Copolymer 345 and Copolymer 937 (copolymers of N-vinylpyrrolidone and t-butylaminoethyl methacrylate of average molecular weight about 1,000,000) and Gafquat<sup>®</sup> 755 and 755N (quaternary ammonium polymers formed by the reaction of dimethyl sulfate and a copolymer of N-vinylpyrrolidone and dimethylaminoethyl methacrylate of average molecular weight about 1,000,000).

According to the present invention there is also required a latex of water-insoluble polymeric particles dispersed in water. Amounts of the particles range from about 1 to about 30%, preferably from about 1.5 to about 10% by weight of the hairspray composition. The average particle size should be no higher than 3 microns, preferably no higher than 1 micron, optimally less than 1 micron. A preferred average diameter size ranges from 0.005 to 1 micron.

A wide variety of homopolymers and copolymers are suitable in forming the latex particles. Vinyl polymerization

derived polymers are preferred rather than condensation polymers (e.g. Eastman AQ type). Monomers which comprise the polymers may be selected from any emulsion polymerizable monomer that contains ethylenically unsaturated groups such as  $\alpha$ -methylstyrene, divinylbenzene, styrene, acrylic acid and  $C_1-C_{12}$  esters, methacrylic acid and  $C_1-C_{12}$  esters, vinyl acetate, crotonic acid and  $C_1-C_{12}$  esters, vinyl neodecanoate, acrylamide, methacrylamide, maleic acid and  $C_1-C_{12}$  esters, and combinations of these. Preferred latices are those of styrene/butyl acrylate, methyl methacrylate/butyl acrylate, vinyl acetate/butyl acrylate and vinyl acetate/methyl methacrylate.

The latex particles are formed by emulsion polymerizing monomers constituting the latex in the presence of the water-soluble polymer held in aqueous media. For purposes of this invention, the term "resin" will mean the aforementioned preferred aspect of the combined latex particles and water-soluble polymer in whose presence the latex was prepared.

Solids content of the latex may range anywhere from about 5 to 60%, preferably 20 to 50%. The ratio of water-soluble polymer to latex particles may range anywhere from about 10:1 to about 1:10 preferably from about 7:3 to about 3:7, optimally from about 2:1 to 1:2 by weight.

The term "water-soluble" refers to any material that has solubility of at least 5 gram per 100 grams of water, i.e. 5%, preferably a solubility of at least 10% by weight. Conversely, the term "water-insoluble" refers to substances that are insoluble at a level of less than 0.1 gram per 100 grams of water, i.e. less than 0.1% by weight.

5 Compositions of the present invention will also include water as a solvent carrier for the polymers and other components. Water will be present in amounts ranging from about 20% to about 99%, preferably from about 40% to about 95% by weight. Optimally, water will be the major if not exclusive solvent, i.e. liquid carrier, for the hair treatment compositions of this invention. Volatile organic solvents such as methanol, ethanol or isopropanol are preferably absent.

10 With certain of the resins it may be necessary to neutralize some acidic groups to promote solubility/dispersibility. Examples of suitable neutralizing agents include  
 15 2-amino-2-methyl-1,3-propanediol (AMPD);  
 2-amino-2-ethyl-1,3-propanediol (AEPD);  
 2-amino-2-methyl-1-propanol (AMP); 2-amino-1-butanol (AB);  
 monoethanolamine (MEA); diethanolamine (DEA);  
 triethanolamine (TEA); monoisopropanolamine (MIPA);  
 20 diisopropanol-amine (DIPA); triisopropanolamine (TIPA); and  
 dimethyl stearamine (DMS). Amounts of the neutralizing agents will range from about 0.001 to about 10% by weight.

25 The present hair treatment compositions may be formulated as sprays in aerosol or nonaerosol forms. If an aerosol hairspray is desired, a propellant must be included in the composition. This agent is responsible for expelling the other materials from the container and forming the hairspray character.

30 The propellant gas can be any liquefiable gas conventionally used for aerosol containers. Preferably the density of the propellant or mixture thereof is less than the hairspray concentrate so that pure propellant is not emitted from the container. Examples of suitable propellants include  
 35 dimethyl ether, propane, n-butane and isobutane, used singly

or admixed. Dimethyl ether is preferred because of its water-solubility up to 35% by weight.

5 The amount of the propellant gases is governed by normal factors well known in the aerosol art. For hairsprays the level of propellant is generally from about 3 to about 50%, preferably from about 5 to about 45%, optimally about 30% of the total composition.

10 Small quantities of surfactant ranging anywhere from 0.1 to about 10%, preferably from about 0.1 to about 1%, optimally about 0.3% by weight may be present in the compositions of the invention. The surfactant may be an anionic, nonionic or cationic emulsifier. Particularly preferred are nonionic  
15 emulsifiers which are formed from alkoxylation of hydrophobes such as fatty alcohols, fatty acids and phenols. Illustrative of such material is Triton X-100, and isooctyl phenyl polyethoxyethanol.

20 Resins when deposited upon hair quite often impart dullness. Counteraction of the dullness effect may be achieved by incorporating low levels of  $C_{12}$ - $C_{22}$  fatty alcohol esters. Particularly preferred is cetearyl octanoate. Amounts of these luster imparting agents will range from about 0.001 to  
25 about 1%, preferably from about 0.01 to about 0.5%, optimally from about 0.02 to about 0.1% by weight.

30 Compositions of this invention may contain any other ingredient normally used in hairsprays. These other ingredients may include antifoam agents, proteins, antioxidants, fragrances, antimicrobials and sunscreens. Each of these ingredients will be present in an amount effective to accomplish its purpose.

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Hairspray formulations of the present invention may, if desired, be packaged in a pump spray container operated without any propellant. Otherwise, the composition may be charged into a suitable pressurizable container which is sealed and then charged with propellant according to conventional techniques.

The following examples will more fully illustrate the embodiments of this invention. All parts, percentages and proportions referred to herein and the appended claims are by weight unless otherwise indicated.

EXAMPLES 1-3Preparation of Latex Resins Based on Styrene/Butylacrylate Latex

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Examples 1 to 3 with the latex resin composition as shown in Table I were prepared as follows: 120 grams (360 grams for Example 3) of deionized water, all the Amphomer LV71 and AMP (aminomethylpropanol) as shown in Table I were added to a 4-neck round bottom glass reactor equipped with temperature controller, nitrogen inlet and outlet, mechanical stirrer and condenser. The reactor was purged with nitrogen gas, heated and maintained at 80°C to dissolve all the Amphomer LV71. Three grams of monomer mixture were charged to the reactor and then 10 grams of 1% potassium persulfate solution were added to start the polymerization. Five minutes after adding the persulfate solution, the remaining monomer mixture was fed to the reactor over a 15 minute period. Thereupon the reaction was maintained at 80°C for another 50 minutes. The emulsion was cooled to room temperature and filtered through a 25 micrometer filter. Particle size, pH, emulsion viscosity and film formation properties were measured and recorded in Table I.

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TABLE I

|                       | EXAMPLE 1 | EXAMPLE 2 | EXAMPLE 3 |
|-----------------------|-----------|-----------|-----------|
| Amphomer LV71         | 10 g      | 10 g      | 30 g      |
| AMP                   | 1.2 g     | 1.2 g     | 3.6 g     |
| Latex Monomer Mixture | 10 g      | 4 g       | 12 g      |
| Styrene               | -         | 6 g       | 18 g      |
| Butylacrylate         |           |           |           |

|  |        |       |         |
|--|--------|-------|---------|
| Particle Size                              | 134 nm | 81 nm | 85 nm   |
| pH   | 6.5    | 6.6   | 6.8     |
| Viscosity* (30 rpm, 11% solid, #1 spindle) | 6 cps  | 6 cps | 7.5 cps |
| Film Formation at room temperature         | No     | Yes   | Yes     |

\*The viscosity of Amphomer LV71 at 11% solid is 12 cps (with LVT #1 spindle at 30 rpm, 30 sec. reading).

Film "hardness or formation", a measure of hair hold capability, was evaluated by evenly applying 2-4 grams of concentrate onto an 8" x 8" glass plate. Samples were allowed to dry overnight to achieve a thick, dry film. Observations of gelling of the film were recorded. Using a sharp-pointed tool, the film was lightly "scratched" upon the glass plate. Observations were then recorded with regard to hardness and brittleness.



EXAMPLES 4-6Evaluation of Latex Resins Based on Styrene/Butylacrylate  
Latex in Zero VOC Hair Spray Formulation

5 Film "rinseability" was evaluated by placing a clean, dry,  
8" x 8" glass plate in a fume hood. The sample hairspray  
was then applied for 10 seconds evenly coating the glass  
plate throughout. After drying at least 1 hour at room  
temperature, a visual observation of clarity, color precipi-  
10 tate or separation, and brittle-cracks in the film were  
noted. A few drops of warm tap water (about 100°F) were  
lightly applied onto the plate. Through light finger action  
the film was caused to lightly dissolve. Texture was noted.  
A ranking for the samples was then performed according to  
15 ease of rinsability (very poor, poor, medium, good, very  
good) in comparison to available controls.

Due to its poor film forming properties, the latex resin of  
Example 1 was not evaluated for hair spray application.  
20 Examples 2 and 3 were formulated in a water-based hair spray  
formula with the composition shown in Table I A. Amphomer  
LV71 was used as the control (Example 6). All these three  
water-based formulas contain 5.5% polymer solid. Properties  
and performance of these hairspray formulas were evaluated  
25 and are summarized in Table II B. The data clearly shows  
that the latex resin of this invention has much better hair  
fixative properties than the water-soluble polymer alone.

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TABLE II A

|                         | Example 4                | Example 5                 | Example 6                        |
|-------------------------|--------------------------|---------------------------|----------------------------------|
| 5 D.I. Water            | 49.02%                   | 73.07%                    | 49.02%                           |
| Latex Resin             | 50.25%<br>Ex. 2<br>(11%) | 26.2%<br>Ex. 3<br>(21.1%) | 50.25%<br>Amphomer LV71<br>(11%) |
| D.C. 190*<br>Surfactant | 0.10%                    | 0.10%                     | 0.10%                            |
| Methyl Paraben          | 0.20%                    | 0.20%                     | 0.20%                            |
| Glydant                 | 0.05%                    | 0.05%                     | 0.05%                            |
| 10 Triton X-100         | 0.20%                    | 0.20%                     | 0.20%                            |
| Cetearyl<br>Octanoate   | 0.03%                    | 0.03%                     | 0.03%                            |
| Fragrance               | 0.15%                    | 0.15%                     | 0.15%                            |
| 15 TOTAL                | 100%                     | 100%                      | 100%                             |

TABLE II B  
Performance

|                        | Example 4     | Example 5     | Example 6     |
|------------------------|---------------|---------------|---------------|
| 5 Curl Strength (g-cm) | 8.4 $\pm$ 1.1 | 6.0 $\pm$ 0.8 | 4.7 $\pm$ 1.0 |
| Curl Retention         |               |               |               |
| 15 minutes             | 83.7%         | 86.9%         | 79.9%         |
| 30 minutes             | 75.5%         | 78.3%         | 70.8%         |
| 10 1 hour              | 71.6%         | 74.5%         | 61.7%         |
| 2 hours                | 67.1%         | 71.2%         | 53.6%         |
| 4 hours                | 65.2%         | 68.7%         | 49.7%         |
| Overnight              | 60.4%         | 64.3%         | 47.3%         |
| Rinseability           | Very Good     | Very Good     | Very Good     |

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EXAMPLES 7-9

20 Preparation of Latex Resins Based on  
Methylmethacrylate/Butylacrylate Latex

The compositions for these Examples are shown in Table III. These compositions include the same monomers (methylmethacrylate/butylacrylate) but have different ratios of Amphomer LV71 (water-soluble polymer) to monomer (hydrophobic emulsion polymer). Preparation is similar to that used for Example 3. A reactor was charged with 290 grams of deionized water, all the Amphomer LV71 and AMP. The solution was heated and maintained at 80°C to dissolve the Amphomer LV71 under a slow stream of nitrogen gas. After dissolving all the Amphomer LV71, five grams of monomer mixture and 10

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grams of 1.2% potassium persulfate solution were added to the reactor to start the polymerization reaction. Five minutes after adding the persulfate solution, the remaining monomer mixture was fed to the reactor over a span of 15 minutes. The reaction was held at 80°C for another 60 minutes. Upon cooling to room temperature, the emulsion was filtered through a 25 micrometer filter for further evaluation. Particle size, pH, emulsion viscosity and film formation properties were determined and are reported in Table III.

TABLE III

|    | EXAMPLE<br>7                          | EXAMPLE<br>8 | EXAMPLE<br>9 |
|----|---------------------------------------|--------------|--------------|
| 5  |                                       |              |              |
|    | Amphomer LV71                         | 26.7 g       | 40.0 g       |
|    | AMP (aminomethyl-<br>propanol)        | 3.2 g        | 4.8 g        |
|    | Latex Monomer<br>Mixture              | 21.3 g       | 16 g         |
| 10 | Methylmethacrylate                    | 32 g         | 24 g         |
|    | Butylacrylate                         |              | 16 g         |
|    | % Solid                               | 21.1%        | 20.8%        |
| 15 | Particle Size                         | 162<br>nm    | 48 nm        |
|    | Viscosity (30 rpm)                    | 66 cps       | 82 cps       |
|    | pH                                    | 6.7          | 6.7          |
| 20 | Film Formation at<br>room temperature | Yes          | Yes          |

EXAMPLES 10-13Hairspray Formulations Containing Latex Resin  
Based on Methylacrylate/Butylacrylate Latex

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Latex resins of Examples 7 to 9 were formulated in water-based aerosol and pump hairspray compositions. Physical properties and performance of these formulations were evaluated by in-vitro tests. Two alcohol-based hairspray formulas, Examples 13A and 13B were used as controls for performance measurements. Compositions of the two alcohol-based products are given in Table VI. The composition, properties and performance of aerosol and pump formulations are summarized in Tables IV and V, respectively.

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TABLE IVWater-Based Aerosol Hairspray5 Formulation

|                          | Example 10         | Example 11         | Example 12         |
|--------------------------|--------------------|--------------------|--------------------|
| D.I. Water               | 44.6%              | 44.5%              | 44.6%              |
| 10 Latex Resin           | 25.0%<br>Example 7 | 25.1%<br>Example 8 | 25.0%<br>Example 9 |
| D.C. 190<br>Surfactant   | 0.07%              | 0.07%              | 0.07%              |
| Triton X-100             | 0.21%              | 0.21%              | 0.21%              |
| 15 Cetearyl<br>Octanoate | 0.02%              | 0.02%              | 0.02%              |
| Fragrance                | 0.10%              | 0.10%              | 0.10%              |
| Dimethylether            | 30.0%              | 30.0%              | 30.0%              |
| TOTAL                    | 100%               | 100%               | 100%               |

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Physical Properties

|   |                    | Example 10 | Example 11 | Example 12 |
|---|--------------------|------------|------------|------------|
| 5 | pH                 | 6.70       | 6.75       | 6.70       |
|   | Viscosity<br>(cps) | 4.5        | 5.0        | 4.5        |

10

Performance

| 15 |              | Example<br>10 | Example<br>11 | Example<br>12 |
|----|--------------|---------------|---------------|---------------|
|    | Hair Holding | Very Good     | Very Good     | Very Good     |
|    | Rinseability | Very Good     | Very Good     | Very Good     |
|    | Gloss        | Very Good     | Very Good     | Poor          |

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25 \*See Table VII for composition.



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TABLE V

Water-Based Pump HairsprayFormulation

|                         | Example<br>10      | Example<br>11      | Example<br>12         |
|-------------------------|--------------------|--------------------|-----------------------|
| D.I. Water              | 73.07%             | 72.97%             | 73.2%                 |
| Latex Resin             | 26.2%<br>Example 7 | 26.3%<br>Example 8 | 26.1%<br>Example<br>9 |
| D.C. 190°<br>Surfactant | 0.10%              | 0.10%              | 0.10%                 |
| Methyl paraben          | 0.20%              | 0.20%              | 0.20%                 |
| Glydant                 | 0.05%              | 0.05%              | 0.05%                 |
| Triton X-100            | 0.20%              | 0.20%              | 0.20%                 |
| Cetearyl<br>Octanoate   | 0.03%              | 0.03%              | 0.03%                 |
| Fragrance               | 0.15%              | 0.15%              | 0.15%                 |
| TOTAL                   | 100%               | 100%               | 100%                  |

Physical Properties

|                 | Example 10 | Example 11 | Example 12 |
|-----------------|------------|------------|------------|
| pH              | 6.75       | 6.6        | 6.6        |
| Viscosity (cps) | 4.2        | 4.0        | 4.2        |

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Performances

|              | Example 10 | Example 11 | Example 12 |
|--------------|------------|------------|------------|
| Hair holding | Excellent  | Very Good  | Good       |
| Rinseability | Poor       | Very Good  | Very Good  |
| Gloss        | Good       | Very Good  | Good       |

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\*See Table VII for composition.

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TABLE VI

EXAMPLE 13A

| INGREDIENT                   | % BY WEIGHT |
|------------------------------|-------------|
| Ethyl Alcohol (SDA 40)       | 74.99       |
| Aminomethylpropanol          | 0.39        |
| NSC Resin 28-2930            | 4.50        |
| Fragrance                    | 0.12        |
| Propellant 50 (Hydro-carbon) | 20.00       |

EXAMPLE 13B

| INGREDIENT             | % BY WEIGHT |
|------------------------|-------------|
| Ethyl Alcohol (SDA 40) | 77.096      |
| D.I. Water             | 16.251      |
| Amphomer 28-4910       | 5.600       |
| Aminomethylpropanol    | 1.023       |
| Fragrance              | 0.030       |

EXAMPLES 14 to 17

Four latex resin compositions with components shown in Table VII were prepared by the same procedure as that used in Examples 7-9. All the latex resin compositions have the same ratio of Amphomer LV71 to monomer mixture but different monomer compositions. These latex resin compositions, except for Example 15 (which had poor film forming properties), were formulated in a water-based aerosol and pump hairspray with the same formulation as shown in Table IV and V, respectively. These compositions were evaluated for hairspray performance. Results are summarized in Table VII. The latex resin of Example 3 was used for comparison.

TABLE VII

## Latex Resin Composition and Properties

|  | Example<br>14 | Example 8 | Example<br>15 | Example<br>16 | Example<br>17 |
|--|---------------|-----------|---------------|---------------|---------------|
| Amphomer LV71                            | 40 g          | 40 g      | 40 g          | 40 g          | 40 g          |
| Methylmethacrylate                       | 12 g          | 16 g      | 28 g          | 0 g           | 0 g           |
| Butylacrylate                            | 28 g          | 24 g      | 12 g          | 0 g           | 8 g           |
| Vinylacetate                             | 0 g           | 0 g       | 0 g           | 40 g          | 32 g          |
| % Solid                                  | 21%           | 20.8%     | 21.1%         | 19.6%         | 19.8%         |
| pH                                       | 6.7           | 6.7       | 6.7           | 6.2           | 6.4           |
| Particle Size                            | 81 nm         | 66 nm     | 72 nm         | 77 nm         | 67 nm         |
| Viscosity (cps)                          | 330           | 82        | 114           | 7             | 8             |
| Film Formation at<br>room<br>temperature | Yes           | Yes       | Yes           | No            | Yes           |

Properties and Performance of Aerosol Hairspray

|                 | Example 14 | Example 8 | Example 15 | Example 16 | Example 17 |
|-----------------|------------|-----------|------------|------------|------------|
| pH              | 6.65       | 6.75      | 6.4        | --         | 6.4        |
| Viscosity (cps) | 4.5        | 5.0       | 5.0        | --         | 3.5        |
| Hair holding    | Very Good  | Very Good | Very Good  | --         | Poor       |
| Rinseability    | Very Good  | Very Good | Very Good  | --         | Very Good  |
| Gloss           | Poor       | Good      | Very Good  | --         | Very Good  |

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Properties and Performance of Pump Hairspray

|                    | Example 14 | Example 8 | Example 15 | Example 16 | Example 17 |
|--------------------|------------|-----------|------------|------------|------------|
| pH                 | 6.6        | 6.6       | 6.8        | --         | 6.45       |
| Viscosity<br>(cps) | 4.0        | 4.0       | 4.5        | --         | 3.5        |
| Hair holding       | Very Good  | Very Good | Poor       | --         | Very Good  |
| Rinseability       | Good       | Very Good | Very Good  | --         | Very Good  |
| Gloss              | Good       | Very Good | Good       | --         | Very Good  |

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EXAMPLES 18-24Specifications

5 The compositions of these Examples are shown in Table VIII. -  
These resins were prepared by adding 280 grams (180 grams  
for Examples 18 and 24) of deionized water, 0.6 grams sodium  
lauryl sulfate (1.0 grams for Examples 18 and 24) and 1.0  
10 grams surfactant combination and 1.2 grams AMP (Examples 19-  
21; 2.4 grams AMP in Example 23) to a 4-neck round bottom  
glass reactor. The reactor was purged with nitrogen gas,  
heated and maintained at 80°C to dissolve all the surfactant  
and water-soluble polymer. Ten grams of the acrylate mono-  
15 mers were added to the reactor followed by 20 grams of 1%  
potassium persulfate solution to start the polymerization.  
Five minutes later, the remaining monomer mixture was fed to  
the reactor over a 40-minute period. Thereupon, the reac-  
tants were heated at 80°C for another 50 minutes. The  
20 resultant emulsion was cooled to room temperature and the pH  
adjusted to 6.0 to 7.0 by neutralization with aminomethyl-  
propanol. Part of the emulsion was physically blended with  
Amphomer LV71 solution (16 weight%) according to the amounts  
shown in Table VIII (second section) to achieve the final  
25 latex resin composition.

The final latex resin compositions were then incorporated  
into a hair setting composition that included an aerosol



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propellant. These formulas are outlined in Tables IX and X.

TABLE VIII

5 Latex Resin

|                    | EXAMPLE (WEIGHT %) |    |    |    |    |    |    |  |
|--------------------|--------------------|----|----|----|----|----|----|--|
|                    | 18                 | 19 | 20 | 21 | 22 | 23 | 24 |  |
| Amphomer LV71      | -                  | 10 | 10 | 10 | -  | 20 | -  |  |
| Polyvinylalcohol   | -                  | -  | -  | -  | 10 | -  | -  |  |
| Butylacrylate      | 56                 | 54 | 54 | 54 | 54 | 48 | 60 |  |
| Methylmethacrylate | 38                 | 36 | 36 | 36 | 36 | 32 | 40 |  |
| Methacrylic Acid   | 6                  | -  | -  | -  | -  | -  | -  |  |

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Physical Blending of Latex Resin with Water-Soluble Polymer

|               |    |     |    |    |    |    |   |
|---------------|----|-----|----|----|----|----|---|
| Latex Resin   | 50 | 100 | 78 | 56 | 55 | 63 | * |
| Amphomer LV71 | 50 | 0   | 22 | 44 | 45 | 37 |   |

\*Coagulate

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Final Latex Resin Composition

|                    |    |    |    |    |     |    |  |
|--------------------|----|----|----|----|-----|----|--|
| Amphomer LV71      | 50 | 10 | 30 | 50 | 45  | 50 |  |
| Polyvinylalcohol   | -  | -  | -  | -  | 5.0 | -  |  |
| Butylacrylate      | 28 | 54 | 42 | 30 | 30  | 30 |  |
| Methylmethacrylate | 19 | 36 | 28 | 20 | 20  | 20 |  |
| Methacrylic Acid   | 3  | -  | -  | -  | -   | -  |  |

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TABLE IX

Pump Hairspray Formulations. Properties and Performance 15.5% resin

| LATEX RESIN COMPOSITION EXAMPLES              |       |       |       |       |       |       |
|---|-------|-------|-------|-------|-------|-------|
| COMPONENTS                                    | 18    | 19    | 20    | 21    | 22    | 23    |
| Water, D.I.                                   | 73.77 | 74.97 | 73.67 | 71.07 | 70.47 | 72.87 |
| Latex Resin Composition %<br>(includes water) | 25.50 | 24.30 | 25.60 | 28.20 | 28.80 | 26.40 |
| Methyl Paraben                                | 0.20  | 0.20  | 0.20  | 0.20  | 0.20  | 0.20  |
| Triton X-100                                  | 0.20  | 0.20  | 0.20  | 0.20  | 0.20  | 0.20  |
| Fragrance                                     | 0.15  | 0.15  | 0.15  | 0.15  | 0.15  | 0.15  |
| DC-190 <sup>®</sup> Surfactant                | 0.10  | 0.10  | 0.10  | 0.10  | 0.10  | 0.10  |
| Glydant                                       | 0.05  | 0.05  | 0.05  | 0.05  | 0.05  | 0.05  |
| Cetearyl Octanoate                            | 0.03  | 0.03  | 0.03  | 0.03  | 0.03  | 0.03  |
| TOTAL   | 100%  | 100%  | 100%  | 100%  | 100%  | 100%  |

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5 Physical Property

|                 | LATEX RESIN COMPOSITION EXAMPLES |      |      |      |      |      |         | ALCOHOL BASE |
|-----------------|----------------------------------|------|------|------|------|------|---------|--------------|
|                 | 18                               | 19   | 20   | 21   | 22   | 23   | Control |              |
| COMPONENTS      |                                  |      |      |      |      |      |         |              |
| pH              | 6.46                             | 6.72 | 6.53 | 6.51 | 6.52 | 6.57 |         |              |
| Viscosity (cps) | 4.0                              | 3.5  | 4.0  | 4.0  | 4.0  | 4.5  |         |              |

10

15 Performance

|                      |            |            |            |            |            |            |            |
|----------------------|------------|------------|------------|------------|------------|------------|------------|
| Hair Hold Capability | Good       | Good       | Fair       | Good       | Very Good  | Very Good  | Very Good  |
| Film Characteristics | Clear/Hard | Milky/Soft | Clear/Hard | Clear/Hard | Clear/Hard | Clear/Hard | Clear/Hard |
| Rinseability         | Very Good  | Good/Fair  | Very Good  | Very Good  | Very Good  | Very Good  | Very Good  |
| Gloss                | Good       | S/Dull     | S/Dull     | Good       | Very Good  | Good       | Very Good  |

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TABLE X

Aerosol Hairspray Formulations. Properties and Performance (5.25% resin)

| COMPONENTS                                 | LATEX RESIN COMPOSITION EXAMPLES |       |       |       |       |       |
|--|----------------------------------|-------|-------|-------|-------|-------|
|  | 18                               | 19    | 20    | 21    | 22    | 23    |
| Water, D.I.                                | 45.09                            | 46.35 | 45.09 | 42.64 | 42.08 | 44.46 |
|  | 24.50                            | 23.24 | 24.50 | 26.95 | 27.51 | 25.13 |
| Latex Resin Composition & (includes water) |                                  |       |       |       |       |       |
| Dimethylether                              | 30.00                            | 30.00 | 30.00 | 30.00 | 30.00 | 30.00 |
| Triton X-100                               | 0.21                             | 0.21  | 0.21  | 0.21  | 0.21  | 0.21  |
| Fragrance                                  | 0.10                             | 0.10  | 0.10  | 0.10  | 0.10  | 0.10  |
| DC-190 <sup>e</sup> Surfactant             | 0.07                             | 0.07  | 0.07  | 0.07  | 0.07  | 0.07  |
| Cetearyl Octanoate                         | 0.02                             | 0.02  | 0.02  | 0.02  | 0.02  | 0.02  |
| TOTAL                                      | 100%                             | 100%  | 100%  | 100%  | 100%  | 100%  |

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Physical Properties

|                    | LATEX RESIN COMPOSITION<br>EXAMPLES |      |      |      |      | ALCOHOL<br>BASE |         |  |
|--------------------|-------------------------------------|------|------|------|------|-----------------|---------|--|
|                    | 18                                  | 19   | 20   | 21   | 22   | 23              | Control |  |
| COMPONENTS         |                                     |      |      |      |      |                 |         |  |
| pH                 | 6.40                                | 6.66 | 6.53 | 6.42 | 6.42 | 6.47            |         |  |
| Viscosity<br>(cps) | 4.5                                 | 4.5  | 4.5  | 4.5  | 4.5  | 5.5             |         |  |

Performance

|                              |                |                |                |                |                |                |            |
|------------------------------|----------------|----------------|----------------|----------------|----------------|----------------|------------|
| Hair Hold<br>Capability      | Good           | Good           | Poor           | Very<br>Good   | Good/<br>Fair  | Good           | Very Good  |
| Film<br>Character-<br>istics | Clear/<br>Hard | Milky/<br>Hard | Milky/<br>Soft | Clear/<br>Hard | Clear/<br>Soft | Clear/<br>Hard | Clear/Hard |
| Rinseability                 | Very<br>Good   | Good/<br>Poor  | Very<br>Good   | Very<br>Good   | Very<br>Good   | Very<br>Good   | Very Good  |
| Gloss                        | Good           | Good           | Dull           | Very<br>Good   | Good           | Good           | Very Good  |

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Examples 24-33 - The effect of polymerising in the presence of resin

5 A series of resin compositions were prepared in the form of  
(1) a water insoluble latex; (2) a latex/water-soluble  
polymer (physical blend); and/or (3) a latex prepared in the  
presence of the water-soluble polymer ("emulsion").

10 The water insoluble latexes prepared included polystyrene,  
polymethyl methacrylate (referred to as PMMA) and  
poly(methyl methacrylate/butyl acrylate). In each instance,  
62.5g monomer (e.g. styrene) was polymerized in a solution  
of 250g water containing 12.5g Igepal CO660® (surfactant),  
0.5g sodium lauryl sulphate and 0.6g potassium persulphate.

15 The latex/water-soluble polymer (physical blend) was typi-  
cally formed by adding 45 g of the latex (22.3% resin) to  
160 g of Amphomer LV-71® solution and mixed for thirty (30)  
minutes.

20 Resins according to the present invention were prepared by  
polymerizing monomer in the presence of Amphomer LV-71® to  
form an "emulsion" resin. For instance, 24g styrene was  
polymerised in 225g water in the presence of 36g Amphomer  
25 LV-71®, 4.32g amino methyl propanol (AMP) and 0.15g potas-  
sium persulphate. The ratio of methyl methacrylate to butyl



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acrylate was 60:40 in the poly(methyl methacrylate/butyl  
acrylate) latex blend and emulsion resin compositions.

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TABLE XI  
PUMP HAIRSPRAY FORMULATIONS

| COMPONENT                             | WEIGHT % |
|---------------------------------------|----------|
| Total Resin Composition<br>(% active) | 5.00     |
| Methyl Paraben                        | 0.10     |
| Triton X-100®                         | 0.20     |
| Fragrance                             | 0.20     |
| DC 190® Surfactant                    | 0.15     |
| Glydant                               | 0.05     |
| Cetearyl Octanoate                    | 0.03     |
| Water                                 | qs       |

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| Example Number | Resin Composition                      | Film Properties | Performance           |               |                  |
|----------------|--|-----------------|-----------------------|---------------|------------------|
|                |  |                 | Gloss/Shine (Clarity) | Hold Capacity | Spray Properties |
| 24             | Amphomer LV-710                        | Very Good       | Clear                 | Very Good     | Poor             |
| 25             | Polystyrene                            | Poor            | Cloudy                | Soft          | -                |
| 26             | Amphomer®/Polystyrene (Physical Blend) | Poor            | Cloudy                | Soft          | -                |
| 27             | Amphomer®/Polystyrene (Emulsion)       | Good            | Clear                 | Good          | Good             |
| 28             | Polymethylmeth-acrylate                | Poor            | Cloudy                | Soft          | -                |
| 29             | Amphomer®/PMMA (Physical Blend)        | Poor            | Clear                 | Soft          | -                |
| 30             | Amphomer®/PMMA (Emulsion)              | Good            | Clear                 | Good          | Good             |
| 31             | Poly (NMA/BA)                          | Poor            | Cloudy                | Soft          | -                |
| 32             | Amphomer®/Poly (NMA/BA) Physical Blend | Good            | Clear                 | Good          | Good             |
| 33             | Amphomer®/Poly (NMA/BA) (Emulsion)     | Good            | Clear                 | Good          | Good             |

Each of the resin compositions was formulated into a pump hairspray formulation as outlined in Table XI. The performance and identity of the resin compositions is outlined under Table XII.

5

Based on the performance results outlined under Table XII, the following conclusions can be made:

10

A water-soluble polymer such as Amphomer LV-710 by itself has very good film properties, very good hair hold capacity and exhibits clear gloss/shine. However, this water-soluble polymer, when used as the sole resin, exhibited poor spray properties. See Example 24.

15

The water-insoluble latex, when used as the sole resin, exhibited poor film properties, provided only a soft hairhold capacity and was unacceptably cloudy. See Examples 25, 28 and 31.

20

A physical blending of the water-soluble polymer and latex provided poor film properties as illustrated by the combination of Amphomer®/polystyrene and of Amphomer®/PMMA. The hairhold capacity was also unacceptably soft for each of these resin compositions. See Examples 26 and 29 respectively.

25

By contrast, the resin compositions wherein styrene and methylmethacrylate were each formed into latexes in the presence of Amphomer®, provided a resultant substance that had good film properties, good hairhold capacity and a clear gloss/shine. These results were unexpected. See Examples 27 and 30.

Poly(methylmethacrylate/butylacrylate) when combined with Amphomer® either in a physical blend or as the "emulsion", provided hairsprays that exhibited good film properties, good hairhold capacity and a clear gloss/shine. See Examples 32 and 33. This contrasts with Example 31 based solely on poly(methacrylate/butylacrylate) as the resin, which exhibited poor film properties, inadequate hairhold capacity and a cloudy gloss/shine.

The foregoing description and Examples illustrate selected embodiments of the present invention. In light thereof, various modifications will be suggested to one skilled in the art, all of which are within the spirit and purview of this invention.

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THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE  
PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. An aqueous hairspray composition comprising:
  - (i) a water-soluble polymer having a solution viscosity  
5 at 10% in water of less than about 20,000 cps at 25°C, the  
polymer being present in an amount from about 1 to about 30%  
by weight.
  - (ii) a latex of water-insoluble polymeric particles dis-  
10 persed in water, the average particle size being no higher  
than about 3 microns, the particles being present in an  
amount 1 to about 30% by weight and wherein the water insol-  
uble polymeric particles are formed from respective ~~monomers~~  
in the presence of the water soluble polymer.
- 15 2. A composition according to claim 1 wherein the  
viscosity of the water-soluble polymer is less than about  
15,000 cps.
- 20 3. A composition according to claim 1 wherein the  
average particle size is no higher 1 micron.
4. A composition according to claim 1 wherein the  
water-soluble polymer is amphoteric.

5. A composition according to claim 1 wherein the ratio of water-soluble polymer to latex particles ranges from about 10:1 to about 1:10 by weight.

5        6. A composition according to claim 1 wherein the ratio of water-soluble polymer to latex particles ranges from about 2:1 to about 1:2.

10       7. A composition according to claim 1 wherein the latex is formed of monomers selected from the group consisting of styrene,  $\alpha$ -methylstyrene, divinylbenzene, acrylic acid and  $C_1$ - $C_{20}$  esters, methacrylic acid and  $C_1$ - $C_{20}$  esters, vinyl acetate, crotonic acid and  $C_1$ - $C_{20}$  esters, vinyl neodecanoate, acrylamide, methacrylamide, maleic acid and esters, and  
15       combinations thereof.

8. A composition according to claim 1 wherein the latex is selected from the group consisting of styrene/butyl acrylate, methyl methacrylate/butyl acrylate, vinyl  
20       acetate/butyl acrylate, methyl methacrylate, vinyl acetate/methyl methacrylate and combinations thereof.

9. A method for setting hair comprising contacting the hair with an aqueous hairspray composition comprising:  
25       (i) a water-soluble polymer having a solution viscosity at 10% in water of less than about 20,000 cps at

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25°C, the polymer being present in an amount from about 1 to about 30% by weight.

- (ii) a latex of water-insoluble polymeric particles  
5 dispersed in water, the average particle size being no  
higher than about 3 microns, the particles being present in  
an amount from about 1 to about 30% by weight and wherein  
the water insoluble polymeric particles are formed from  
respective monomers in the presence of the water soluble  
10 polymer.



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10. An aqueous hairspray composition as claimed in claim 1  
and substantially as described herein.